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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
MESTACH, D. et al.

Serial No.: 10/620,939
Filing Date: July 15, 2003

Title: METHOD FOR MAKING METHACRYLATE
UNIT-CONTAINING LOW-POLYDISPERSITY
POLYMERS

Commissioner for Patents
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Lynn Brush
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SUBMISSION OF CERTIFIED PRIORITY DOCUMENT

Enclosed herewith is a certified copy of European Patent Application No. 02078004.5, to support the claim of foreign priority benefits under 35 U.S.C. §119 in connection with the above-identified application.

Respectfully submitted,

Michelle J. Burke
Attorney for Applicant(s)
Reg. No. 37,791

Akzo Nobel Inc.
Intellectual Property Dept.
7 Livingstone Avenue
Dobbs Ferry, NY 10522-3408
(914) 674-5459





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Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

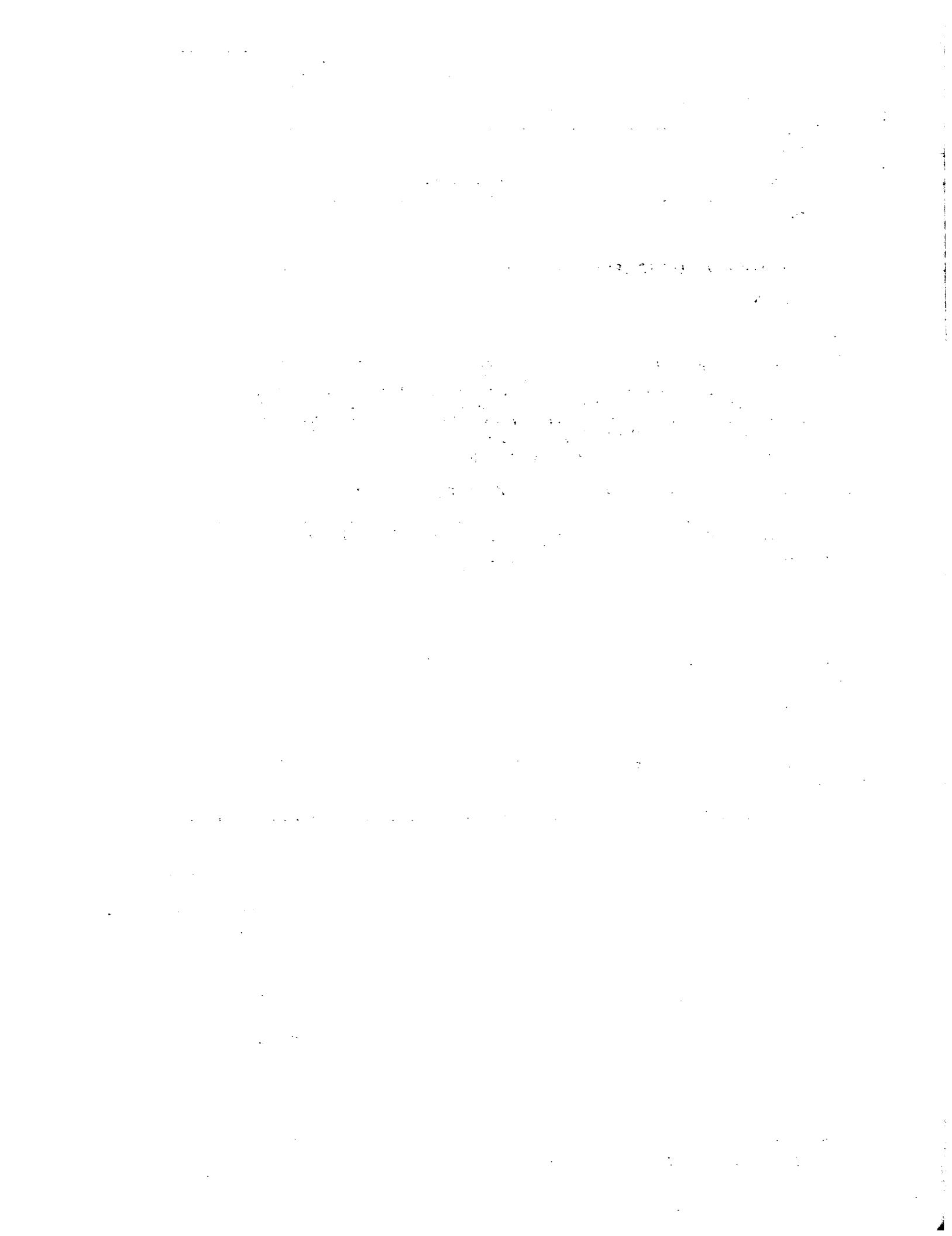
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Der Präsident des Europäischen Patentamts:
im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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R C van Dijk





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Akzo Nobel N.V.
Velperweg 76
6824 BM Arnhem
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Method for making methacrylate unit-containing low-dispersity polymers

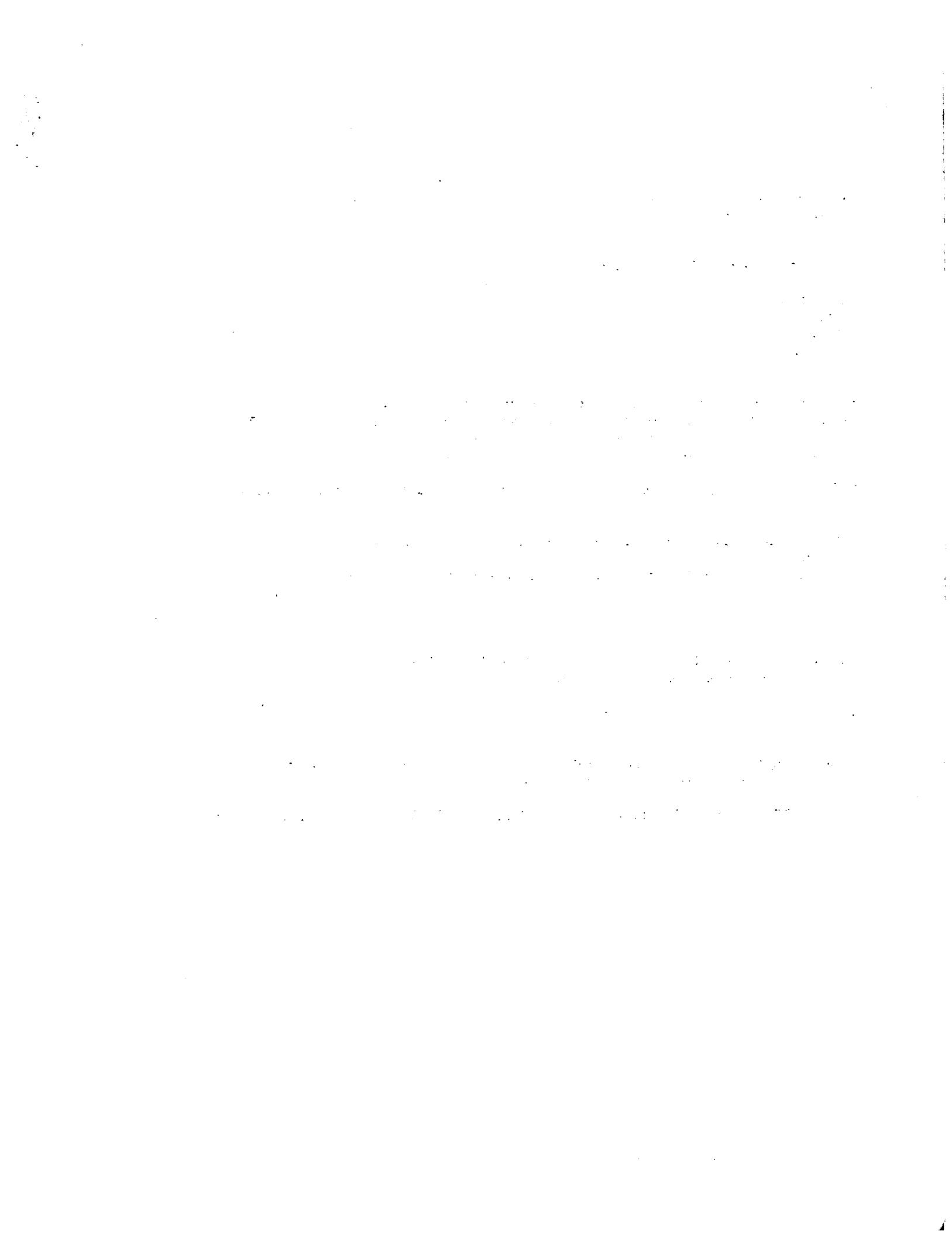
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METHOD FOR MAKING METHACRYLATE UNIT-CONTAINING LOW-DISPERSITY POLYMERS

The invention pertains to a method for making a methacrylate unit-containing polymer with dispersity <1.7 and containing at least one cross-linkable functional group.

- 5 Polymers with narrow molar mass distribution have benefits for cross-linkable compositions containing monomers with functional side groups, in that a narrower molar mass distribution will lead to narrower functionality distributions. Broad functionality distributions are detrimental to the properties of coatings formulations, especially if rather low-molecular weight, high functionality side raises the viscosity and limits the "pot life" of so-called two-component formulations, whereas the low-molecular weight low functionality side may contribute to the formation of so-called dead-ends 10 and extractable materials, which limit the properties of the cross-linked films 15 to be formed.

Narrow-dispersity functional polymers have been prepared and described for other so-called "living" (or "controlled") radical polymerizations.

- 20 In the field of "living" radical polymerizations (polymerizations under radical conditions where termination processes of growing radicals are reversible, so that all initiated chains can in principle continue growing as long as monomers and radicals are present), three technologies have been studied in depth:
 - 25 - *nitroxide mediated polymerizations* (NMP), which are based on homolytic scission of the covalent bond formed between a polymer radical and a nitroxide stable radical;

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- *atom transfer radical polymerization* (ATRP), in which a halogen (usually Cl or Br) atom is reversibly transferred between a Cu(I/II) complex and a polymer radical, in a process that encompasses a redox cycle;
- *reversible addition fragmentation chain transfer* (RAFT), which is a process wherein dithioester end groups can be rapidly and reversibly transferred between polymeric radicals.

For all these systems, the living character was proven by a typically linear development of molecular weight with conversion, low polydispersities obtained in polymerizations, and the preparation of block copolymers by sequential addition of different monomers.

Especially ATRP and RAFT have possibilities for numerous applications with respect to the type of monomers used. In ATRP, however, acidic conditions and monomers create problems, whereas the necessary removal of the Cu-amine complexes from the polymers is an expensive and thus unwanted step. In RAFT, these limitations do not occur, but this method suffers in that the polymer chains formed contain dithioester end group, which are strong chromophores. The chromophores can be destroyed by reaction with a nucleophile, which is not always compatible with the functional groups that may be present in the chains, but this is at the expense of an extra reaction step, and leads to low-molecular weight products in the polymer, which may be difficult to remove. Moreover, the dithioester mediating compounds are expensive.

NMP has the disadvantage that expensive nitroxides are needed if the process is to be used at acceptably low temperatures for acrylates, whereas methacrylates have intrinsic problems due to the fact that disproportionation as side reaction may occur.

Another type of living radical polymerization process is *degenerative iodine transfer* (DIT) (see for instance, Journal of Physical Organic Chemistry, vol. 8, pp. 306-315 (1995) and Macromolecules, 28, pp. 8051-8056 (1995)). In this case, similarly to the RAFT process, an iodine end group transfers to

another polymeric radical, the iodine atom playing a similar role as the dithioester group in RAFT. A chain transfer agent with an iodine atom is used as entry in the DIT process. In general, however, RAFT is considered to be superior to DIT in the rate of end group transfer (more transfer events, 5 lower polydispersity, better control), and its applicability to a broader range of monomers.

DIT was described in Macromolecules, 28, pp. 8051-8056 (1995); Macromolecules, 33(9), p. 3485 (2000); Macromolecules, 32(22), p. 7354 (1999); Macromolecules, 31(9), p. 2809 (1998) for application with styrene monomers, for which it appears to work moderately well (dispersities typically 1.5); for halogenated vinyl monomers like vinyl chloride and fluorinated vinyl species. For acrylates it has been attempted, but results for acrylates showed less control (broader polydispersities >2, indicating a low 15 rate of transfer between acrylate chains) (see: Macromolecules, 28, pp. 8051-8056 (1995)). Processes where acrylates are mentioned in combination with iodine transfer, however, sometimes aim more at obtaining iodine functional chains than on actual living polymerizations (see for instance US 6143848). Block copolymers of acrylates and styrene have 20 been reported in EP 947527, Macromolecules, 28, p. 2093 (1995), and Macromol. Rapid Commun., 2000, 21(13), p. 921.

A few attempts to obtain a degenerative iodine transfer process with methacrylates have been reported, but all of these suggest that methacrylate 25 monomers cannot be used in an acceptable manner in conventional DIT processes using the conventional iodine-functional CTA's (alkyl or perfluoroalkyl iodides), which are applied in the DIT process for e.g. styrene (see for instance Macromolecules, 28, p. 8051 (1995)). High-molecular weight material is formed in the beginning of the polymerization, leading to 30 high polydispersities, without observation of the typical linear development of molecular weight with conversion, which is characteristic for a polymerization with a living character. Another comparison of DIT

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processes with styrene, acrylate, and methacrylate monomers are disclosed in L. Klumperman at the UNESCO School & South African IUPAC conference on Macromolecular and Materials Science, 29-31 March 1999 and 10-12 April 2000 to be found at

5 <http://www.sun.ac.za/unesco/PolymerED2000/Conf1999/Lectures1999/Klumperman2.pdf> and
www.sun.ac.za/unesco/PolymerED2000/Conf2000/KlumpermanC.pdf. For these reasons DIT is disclosed not to be suitable for polymerizing methacrylates. In US 5439980 this was confirmed in comparative example 2

10 where it was found that when MMA alone is used with an iodide-functional perfluoropolyether, only a homopolymer of MMA is produced and a block polymer with a perfluoropolyether is not produced.

Since methacrylates are a very important class of monomers for many applications, with high and low polarity candidates, and various functional side groups available, with high Tg backbones being formed with good chemical durability, the inability to use methacrylates is a serious omission in the DIT technology, and a need exists for an effective DIT method allowing the production of polymers based on methacrylates with structures

15 that harvest the advantages of the living nature of the polymerization process.

According to the present invention it was found that a DIT process using methacrylates can be performed in a very favorable way, if the proper start-up process is chosen. When using such start-up process, it was found that a methacrylate-based process shows all characteristics of a living polymerization (i.e., narrow polydispersity, typical linear development of MW with conversion), with a better level of control than reported for acrylate or styrene based DIT processes. It is therefore also an objective of the present

25 invention to obtain a DIT process that can be used for polymerizing methacrylate monomers. This objective was reached by a DIT process in a manner of obtaining a high transfer rate of iodine atoms between

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methacrylate chain ends, leading to better control than DIT of styrenic monomers, to low polydispersities closely resembling that of ATRP or RAFT processes, molecular weights increasing with conversion, and the opportunity to prepare well defined block and gradient methacrylate-containing copolymers.

It has now been realized that polymers obtained by polymerizing methacrylic monomers in the presence of iodine (or iodine-containing chain transfer agents) can be made if the method for polymerization is performed according to the method of the present invention. According to this invention a method was developed for making a methacrylate unit-containing polymer with dispersity <1.7 and containing at least one cross-linkable functional group comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers to a polymer comprising at least 50 mole% of methacrylate units, in the presence of a) a radical precursor and b) I₂ or a sulfonyliodide.

The polymerization reaction of methacrylate monomers in the presence of molecular iodine as such is disclosed in an article by A.A. Lissi and J. Aljaro in Polymer Letters Edition, vol. 14, pp. 499-502 (1976). In this reference it was disclosed that iodine is an efficient inhibitor of the radical polymerization reaction of vinyl acetate, allyl acetate and methyl methacrylate. The reaction with methyl methacrylate was performed with the common radical precursor azobisisobutyronitrile (AIBN) to give a polymer of unknown dispersity. Excessive amounts of radical precursor with respect to iodine were used. The polymer of Lissi et al. was made for theoretical reasons only and did not have a functional group for cross-linking. However, no disclosure or suggestion was made to apply this method in DIT or living radical polymerization processes, and no practical application of this polymer was given.

The low dispersity of the polymers of the invention is important for coating formulations with a good balance of pot life and curing speed, viscosity and network properties. Preferably the dispersity is < 1.5, most preferably < 1.35. The functional group for cross-linking, on the other hand, is essential 5 when making polymeric networks.

The radical polymerization is performed in the presence of iodine or a sulfonyliodide. In the latter case an aromatic sulfonyliodide, more specifically p-toluenesulfonyliodide is preferred.

10 The polymers of the invention can be used in a cross-linkable composition for making a polymeric network, either through self-condensation of the functional groups, or through reaction with an additional cross-linking compound.

15 The novel method also pertains to a process of making iodine-functional methacrylate end group oligomers, which can be used as such to make a cross-linked network or can be used in a DIT process proceeding with a high level of control.

20 To this end the invention also pertains to the above method for making a block or gradient methacrylate unit-containing copolymer with low dispersity.

25 The polymer of the invention can also be a di- or multi-block or gradient copolymer through either the use of monomers with differing polymerization reactivities, or by monomer feeding strategies, as is known to the person skilled in the art.

When molecular iodine is used, the iodine radical released after one iodine 30 is abstracted by a polymer radical does not reinitiate a methacrylate polymerization, but recombines with another polymer radical. The net effect of molecular iodine is the functionalization of two polymer chains with an iodine end group, in an identical way (J. Polym. Sci. Polym. Lett. Ed., vol.

14, p. 499-502 (1976)). In terms of the polymerization process, it implies that slightly more than 1 equivalent of initiating radicals should be generated, compared to iodine atoms present in the systems as molecular iodine. Preferably, the amounts are selected so that the mole ratio I_2 : radical precursor is between 0.05n and 0.5n, wherein n stands for the number of radicals effectively generated per molecule radical precursor. In the case of the use of a sulfonyl iodide chain transfer agent, the preferable mole ratio sulfonyliodide : radical precursor is > 0.1n, preferably > 0.5n.

5 10 The DIT polymerization process of methacrylates takes places at temperatures of less than 130°C, preferably less than 110°C, most preferably less than 90°C. It is preferred that mild initiating radicals are used (e.g. C-centered radicals from azo radical initiators) such as azobisisobutyronitrile (AIBN).

15 20 It may be advantageous to modify the iodine-end groups containing polymers formed in the process according to the invention in a process after or during the polymerization. The end groups can be modified, e.g. by elimination, cyclization, atom transfer, redox, or substitution reaction, optionally under removal of iodine and/or low-molecular weight iodine-containing compounds. If this is done under conditions wherein the polydispersity remains < 1.7, the product so obtained can be used as described above.

25 30 The polymerization process can take place in a batch mode, or in a semi-batch mode, with feeding of several of the reactants to the vessel, or in a process comprising a continuous step. This polymerization can be carried out in bulk, in solvent, in a suspension polymerization process, an emulsion polymerization process, a dispersion polymerization process, or a mini-emulsion polymerization process.

Preferred polymers have Mn < 10,000, more preferably < 5,000, most preferably < 3,500.

The polymers to be formed using the iodine-donating compounds as described, must contain methacrylate units, i.e. containing at least 50 mole% of a methacrylate unit. The other co-monomers may be of the acrylate, styrene, vinyl ester, and maleate type. More preferred is a composition containing at least 70 mole% of methacrylate units, most preferred is a composition having at least 90 mole% of methacrylate units.

Suitable mixtures for making the iodine atom-containing polymer comprise monomers selected from acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, glycidyl methacrylate, glycidyl acrylate, 2-hydroxyethyl acrylate, 2-ethylhexyl acrylate, potassium methacrylate, cyclohexyl methacrylate, 2-(dimethylamino)ethyl methacrylate, stearyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl methacrylate, benzyl methacrylate, lauryl methacrylate, acrylamide, acrolein, methacrylamide, methacrolein, acrylonitrile, methacrylonitrile, styrene, methylstyrene, chlorostyrene, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, vinyl chloride, vinyl trichlorosilane, vinyl trimethoxysilane, vinyl trimethylsilane, butadiene, isoprene, chloroprene, maleic acid, maleimide, methyl maleate, ethyl maleate, propyl maleate, butyl maleate, calcium maleate, allyl maleate, 2-ethylhexyl maleate, octyl maleate, maleic hydrazide, maleic anhydride, fumaric acid, methyl fumarate, ethyl fumarate, propyl fumarate, butyl fumarate, sodium fumarate, fumaronitrile, fumaryl chloride, vinyl acetate, tert-decanoic acid ethenyl ester (VeoVa 10, ex Resolution Performance Products), neononanoic acid ethenyl ester (VeoVa 9, ex Resolution Performance Products), vinyl pivalate, and the like.

It was found to be sometimes advantageous to perform the polymerization in the presence of an epoxide-containing compound. In the presence of epoxide-containing compounds the polydispersity obtained is narrower. Such compounds are preferably selected from glycidyl ethers, glycidyl 5 esters, and cycloaliphatic epoxides. Suitably glycidyl-containing monomers are used in the preparation of the iodine atom-containing polymer, such as the above mentioned glycidyl methacrylate and glycidyl acrylate. The method according to the invention is preferably performed such that the mole ratio epoxide : iodine atom-containing polymer is > 0.01.

10

Examples of functional monomers for cross-linking are ethylenically unsaturated compound containing a second group for cross-linking with a co-reactive compound. The choice of the co-reactive compound that is added to the polymer and that can react with the functional group of the 15 polymer depends on the chemical nature of this group. This compound may either be a polymeric or a low-molecular weight compound. In order to effect cross-linking the cross-linking compound must posses at least two co-reactive groups.

Examples of suitable co-reactive groups for given pendant functional groups 20 are known to the skilled persons. Non-limiting examples are given in Table I.

Table I

Pendant functional group	Co-reactive groups
Carboxylic acid	Oxirane, carbodiimide, aziridine, azetidine, oxazoline
Oxirane	Carboxylic acid, amino, thiol
Hydroxy	Methyol, etherified methyol, isocyanate, aldehyde
Acetoacetoxy	Amino
Amino	Acetoacetoxy, oxirane, aldehyde, ketone, isocyanate
Ketone	Amino, hydrazide
Aldehyde	Amino, hydrazide
Isocyanate	Hydroxy, amino, thiol
Oxazoline	Carboxylic acid

Examples of monomers with carboxylic acid functionality are acrylic and methacrylic acid. Optionally, the acid groups are latent as, for example, in maleic anhydride, where the acid-functionality is present in the form of an anhydride group. Other possible carboxylic acid-functional monomers are
5 oligomerized acrylic acids such as β -carboxyethyl acrylate or its higher analogues (commercially available from Rhodia as Sipomer® B-CEA), itaconic acid, fumaric acid, maleic acid, citraconic acid, or the anhydrides thereof. Also adducts of a hydroxyfunctional monomer and an acid anhydride such as for example the adduct of hydroxyethyl methacrylate and
10 hexahydrophthalic anhydride can be used.

Examples of monomers comprising an amine-functionality are dimethylaminoethyl (meth)acrylate and tertiary-butyl aminoethyl (meth)acrylate.

Amine functionality can also be introduced into the polymer by post reaction
15 of the carboxylic acid group derived from the copolymerization of a functional monomer such as acrylic or methacrylic acid with ethylene imine or propylene imine. Also acetoacetoxy groups from the copolymerization of for instance acetoacetoxy ethylmethacrylate can be reacted with poly(ethyleneimine) to obtain amine functionality. A class of primary amine
20 functional monomers has been described recently and includes aminoethyl, 3-amino-1-propyl, 5-amino-1-pentyl, 6-amino-1-hexyl and 11-amino-1-undecyl methacrylate. Optionally, these monomers can be used as their salts, for example with HCl.

Examples of monomers with oxirane functionality are glycidyl acrylate and
25 glycidyl methacrylate.

Examples of hydroxy-functional monomers for cross-linking are acrylate esters having a hydroxy group such as hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, and the like.

30 Also adducts of hydroxy-functional monomers with ethylene or propylene oxide can be present in the monomer composition.

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Also monomers having latent hydroxy groups, such as glycidyl (meth)acrylate can be used.

Another suitable class of functional monomers for cross-linking is ketone-functional monomers, such as the acetoacetoxy esters of hydroxyalkyl acrylates and methacrylates, such as acetoacetoxyethyl (meth)acrylate, and keto-comprising amides such as diacetone acrylamide.

Examples of isocyanate functional monomers are: benzene, 1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl) (m-TMI from Cytec) and 2-isocyanatoethyl methacrylate (Karenz MOI from SHOWA DENKO). Also adduct made from hydroxy-functional monomer and a di- or triisocyanate can be used, for example the adduct of hydroxyethyl methacrylate and isophorone diisocyanate.

An example of an oxazoline functional monomer is 2-isopropenyl-2-oxazoline.

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The invention is further illustrated with the following examples.

All reported molecular weights were determined by size exclusion chromatography (RI detection), and expressed in polystyrene equivalent molecular weights, unless specified otherwise. Low-molecular weight materials ($M < 500$), originating e.g. also from initiator in cage recombination products and optionally added low-molecular weight epoxides, were not taken into account for this determination of the main polymer envelope in the molecular mass distribution. The following abbreviations are used: MMA = methyl methacrylate, ; BMA = n-butyl methacrylate, HMMA = hydroxymethyl methacrylate, GMA = glycidyl methacrylate; BA = butyl acrylate, SEC = size exclusion chromatography.

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Example 1

A reaction vessel was charged with 11.01 g of MMA, 11.00 g of BMA, 8.06 g of HMMA, 20 g of BA, 1.523 g of I₂, and 2.26 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 7 h. SEC analysis of a sample taken after this period (conversion 98%) yields an Mn 4800, an Mw/Mn of 1.26, and an Mz/Mw of 1.31.

10 Example 2

To a reaction vessel, maintained at 65°C, over a period of 2 h, a solution was fed consisting of 36.49 g of BMA, 6.57 g of GMA, 3.69 g of I₂, and 5.42 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 16 g of Dowanol PM (solvent) to obtain a first BMA-co-GMA block of Mn 2880, Mn/Mw 1.25, Mz/Mw 1.19.

15

Example 3

A reaction vessel was charged with 11.02 g of MMA, 11.01 g of BMA, 20.06 g of BA, 1.52 g of I₂, and 2.26 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was monitored until the dark iodine color starts to fade (conversion 9%). At this point, 5.29 g of methacrylic acid and 2.75g of Cardura E-10 epoxide were added in one shot and the reaction was continued for 4 h. SEC analysis of a sample taken after this period (conversion 99%) yields an Mn 2928, an Mw/Mn of 1.32, and an Mz/Mw of 1.28.

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CLAIMS

1. A method for making a methacrylate unit-containing polymer with dispersity <1.7 and containing at least one cross-linkable functional group comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers to a polymer comprising at least 50 mole% of methacrylate units, in the presence of a) a radical precursor and b) I₂ or a sulfonyliodide.
5
- 10 2. The method according to claim 1 wherein the radical polymerization is performed in the presence of an aromatic sulfonyliodide, preferably p-toluenesulfonyliodide.
- 15 3. The method according to claim 1 or 2 wherein the temperature during the polymerization steps is lower than 130°C, preferably lower than 110°C, and most preferably lower than 90°C.
- 20 4. The method according to any one of claims 1-3 wherein the mole ratio sulfonyliodide : radical precursor is >0.1n, wherein n stands for the number of radicals effectively generated per molecule radical precursor, or wherein the mole ratio I₂ : radical precursor is between 0.05n and 0.5n.
- 25 5. The method according to any one of claims 1-4 wherein the polymerization is performed in the presence of an epoxide-containing compound.
- 30 6. The method according to any one of claims 1-5 wherein the mole ratio epoxide : iodine atom is > 0.01.

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7. The method according to any one of claims 1-5 wherein the mole ratio epoxide : iodine atom is at least 0.05.
- 5 8. The method according to any one of claims 1-7 for making a block or gradient copolymer.
9. The method according to any one of claims 1-8 wherein the iodine atom of iodine-containing end groups is modified.
- 10 10. Use of the polymer obtained according to claim 1-9 in a cross-linkable composition for making a polymeric network.

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ABSTRACT

The Invention pertains to a method for making a methacrylate unit-containing polymer with dispersity <1.7 and containing at least one cross-linkable functional group comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers to a polymer comprising at least 50 mole% of methacrylate units, in the presence of a) a radical precursor and b) I₂ or a sulfonyliodide.

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